

1918
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A STUDY OF THE ARCING OF SILVER IN
SOLUTION OF HALIDES

BY

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THESIS

FOR THE DEGREE

OF

BACHELOR OF SCIENCE
IN CHEMICAL ENGINEERING

THE COLLEGE OF LIBERAL ARTS AND SCIENCES

OF THE

UNIVERSITY OF ILLINOIS

1918

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UNIVERSITY OF ILLINOIS

.....May 28,.....1918..

THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

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* The experimental work for this thesis was originally in charge of Dr. C. R. Engelder. Later, a more specific line was taken up under Dr. H. E. Eastlack.

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A STUDY OF THE ARCING OF SILVER IN SOLUTIONS OF HALIDES

I. INTRODUCTION

A. Nature of Colloidal Silver and Photosalts of Silver.

The action of light upon silver chloride has been known for a long time. Various explanations have been given for the darkening of the compound, such as the formation of a subhalide, the formation of a double salt of the subhalide and the normal halide, and the formation of an adsorption compound of colloidal silver with the photohalide. All theories have had many exponents and each advocate has had his own experimental work to support his assertions. The latest results of the work in photochemistry and colloid chemistry, such as that carried on by Luppo-Cramer¹, seems to show that the adsorption of colloidal silver is the most plausible explanation for the darkening of the halides of silver under the action of light and some reducing agents. The halides of silver are not alone in this property of forming what L. Cary Lea² has called "photo-salts". An instance of this is the discovery of colloidal silver by Wöhler³, who found that in subjecting white silver tartrate to the action of hydrogen at 100° C., he obtained a brown mass which was identified by later investigators as the "phototartrate". Upon treatment with water, however, the silver tartrate dissolved, giving a deep red solution, which he called the "subtartrate" but which we now know as colloidal silver. He explained the gradual

deposition of silver as the decomposition of the subtartrate into the normal tartrate and colloidal silver, which really is very plausible, or at least was at that time. Various other silver salts are capable of adsorbing silver to give colored adsorption compounds.

These photosalts and the photohalides have been analyzed and were seldom found to conform to any simple molecular formula or even to check with themselves. Before the days of colloid chemistry, this was explained by assuming the formation of a solution of the subsalt in the normal salt. L. Carey Lea² was an advocate of this theory and compared the photosalts to the lakes formed in dyeing. After colloidal silver was better understood, he finally adopted the present view by substituting colloidal silver for the silver subsalt in his former theory.

The photohalides of silver according to Carey Lea have the property of assuming many different colors. The chloride shows the greatest variation, the bromide next, and the iodide the least. Silver fluoride does not form a photofluoride although silver subfluoride has been prepared electrolytically according to Guntz⁴. It is yellow and is decomposed by the action of water. Hence silver photohalides must be limited to the chloride, bromide, and iodide. The formation of these various colors is difficult to control or repeat. The directions for the chemical preparation of the photohalides give the exact concentrations that should be employed, and even following them, the effects are difficult to get.

B. Review of Previous Work upon the Photohalides.

The first and probably the greatest amount of work done upon the photohalides was done by L. Carey Lea². He prepared the photohalides by many chemical methods and also studied the various "allotro-

pic" modifications of colloidal silver. He used hypophosphites, ferrous sulphate, etc. to reduce the normal chloride and also used ferric chloride and other oxidizing agents to oxidize finely divided silver. He obtained almost every color of photohalide excepting green, and studied their action under light, mechanical strain, and various other conditions.

Later work has been done by Reinders⁷ and by Trivelli.¹³ These two men held opposite views concerning the theory of the photohalides. Reinders held the view of adsorption, while Trivelli contended that the compounds were subhalides of silver.

Measurement of potentials of the photohalides has been done by Sichling¹⁴ and by Baur.¹⁵ Their results seem to confirm the adsorption theory.

Work has also been done by Lüppe-Cramer¹⁶. A good review of the work of Carey Lea is given in a compilation of his papers by Lüppe-Cramer, entitled "Kolloides Silber und die Photohaloide" (1908).

C. Scope of the Present Investigation.

This investigation was undertaken primarily for the purpose of studying these notable phenomena and also of studying incidental effects in the arcing of silver by the Bredig¹⁷ process using extremely dilute solutions of halides.

In the preliminary work a few photohalides were prepared after studying the preparation and properties of various silver sols. Chemical methods were employed using reducing solutions and silver nitrate. After this, electrical methods were investigated. At first it was thought necessary to use solutions of chlorine, bromine, and iodine, but by experiment it was found that there was enough ox-

idation of the silver in halide solutions alone. By this means the most intimate mixture possible of practically pure colloidal silver, the silver halide, and the electrolyte added or resulting from the reaction, was obtained. No organic or other matter was present as is the case when photohalides are prepared using tartrate solutions. By immediate filtration it is possible to hold most of the substance in solution and separate off the coarse particles. The greater part of the photohalide precipitates in from several minutes to several hours or even days, depending upon the halide used and the concentration. Due to lack of time, however, no other study of the precipitated photohalide was made except to note its color. The color of the solutions was observed both in reflected and transmitted light before and after precipitation.

II. EXPERIMENTAL PART

A. Preliminary Work.

The object of the preliminary work was to study the formation and properties of colloidal silver and to prepare a few of the photohalides of silver by chemical means. Various reducing agents were tried with solutions of silver nitrate and also of silver hydroxide.

The first reducing agent tried, hydrazine sulphate in ammonia, gave varied and uncertain results. Most of the time the silver was precipitated in a black or even grey metallic form. The hydrazine sulphate was diluted and added to dilute silver nitrate, but this made very little difference. By extreme dilution, a yellowish coloration was given to the solution, but this was very unstable.

Formaldehyde solution was then tried. This gave black silver when concentrated, but by diluting, a coarse but stable colloid was obtained which did not dissolve in dilute ammonia. It was bluish purple by transmitted light and had a murky tan color by reflected light.

Ferrous sulphate was tried. In acid solution it gave a grey precipitate of silver, while in alkaline solution the precipitate was black.

Good results were obtained using a mixture of ferrous sulphate, sodium citrate, and a little NaOH, with silver nitrate solution. A clear ruby red solution was first obtained together with grey silver powder. This solution in a few minutes became brown by transmitted light and showed a greenish brown fluorescence by reflected light. After standing several months it had not changed further. Similar results were obtained using Rochelle salts in place of sodium citrate. The stability here is supposed to be due to the formation of gum arabic or a similar organic protective colloid¹⁰ by the oxidation of the citrate or tartrate radical by the silver nitrate.

Following this, hydrazine hydrate was prepared by double decomposition of $\text{Ba}(\text{OH})_2$ and $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4$, precipitating the excess $\text{Ba}(\text{OH})_2$ by CO_2 , and then boiling and filtering. This gave the same results as with hydrazine sulphate in concentrated solution, but when diluted and used with a weakly ammoniacal solution of Ag_2O , it gave a solution, which was reddish brown by transmitted light and showed a greenish opalescence by reflected light. This was stable and had not changed after four months.

The next study was made using dextrin. With dilute dextrin and

a little ammonia, silver nitrate gave a precipitate which was purplish blue by transmitted light and a murky tan by reflected light. It dissolved, however, upon shaking, so it must have been silver oxide. By using very concentrated dextrin and silver nitrate, solutions were obtained which were opaque and fluorescent and looked like the heaviest grades of lubricating oil.

The best results were obtained, however, by treating well washed Ag_2O , precipitated from AgNO_3 by NaOH , with solid dextrin and adding distilled water. After a short time a dark solution was obtained which was a clear reddish brown by transmitted light and showed a greenish brown fluorescence by reflection. In several hours this became opaque and in several days it looked exactly like caramelized milk sugar, and had to be diluted about 100 times to show the color it had in the first few minutes. It requires several weeks to be precipitated by concentrated NaOH , but either concentrated NH_4OH or a 1 : 1 solution of H_2SO_4 will bring down the silver in a few hours. It was entirely soluble in water after evaporation to dryness on a steam bath.

Such a solution, made by decanting the liquid above a mixture of Ag_2O , solid dextrin, and water, that had stood several weeks in the dark in brown bottles, was analyzed for colloidal silver. A five cc. portion was diluted with water to 50 cc. and 10 cc. concentrated NH_4OH with a little H_2SO_4 was added. After standing in a dark cupboard for a day the silver had coagulated as a fine black precipitate, leaving a colorless solution. This was filtered, washed with NH_4OH and dissolved in HNO_3 . It was then titrated by the Volhard method and showed 0.0308 g of silver. The concentration of colloidal silver in the dextrin solution was therefore 6.16 grams

per liter. Silver oxide was retained in solution by the NH_4OH , and was not given an opportunity to be decomposed by light.

Another experiment tried was passing hydrogen into a solution of $\text{Ag}(\text{OH})_2$ which was kept at $55-60^\circ \text{C}$. This gave a greenish solution which precipitated in a day giving a fine black deposit.

The preparation of the photochloride and photobromide was next undertaken. Photohalides have been prepared by two methods, the reduction of the normal halide, and the oxidation of finely divided silver by means of the halogen. The photohalide when prepared by reducing agents is usually very dark purple or even black at first, but after washing with warm dilute nitric acid part of the silver is dissolved and leaves the photohalide showing its particular color. The silver which gives the color can be dissolved out only by concentrated nitric acid. It also is left behind in the metallic state by treating with strong ammonia in the case of the chloride and bromide. This property of the passivity of the silver remaining in the halide is characteristic of adsorbed substances in general as was shown by Linder and Picton⁸ in the case of sulphide sols and by Duclaux⁹ with copper ferrocyanide.

The photochloride was prepared by adding an excess of AgNO_3 to a solution of KCl and then immediately adding ferrous sulphate and NaOH . The mass was dark purple. It was washed with water and with warm HNO_3 (1 : 1), after which a light lilac color developed. Upon repeating the above experiment, the resulting color was pink.

The photobromide was prepared in the same way giving at first a dark purple precipitate and finally after treating with HNO_3 , a deep lilac color.

The action of daylight on these photohalides was the same as

the effect upon the normal halides, the color being a dark lilac, the bromide slightly darker than the chloride. The original color was restored by stirring.

Another effect noticed in this work was the formation of "allotropic" silver mentioned by Carey Lea¹¹. By adding NaOH to the dextrin solution of colloidal silver, and allowing to stand blue silver was deposited as a mirror; and where the solution had evaporated the gold modification was deposited. These have been shown by Lüdtk¹² to be colloidal silver.

This series of experiments showed that colloidal silver is a substance which is unstable in the presence of excessive quantities of electrolyte, but can be prepared easily by using a protective colloid. It also demonstrated that photohalides can readily be prepared, but that their color is variable.

B. The Bredig Process for Silver in Halide Solutions.

This part of the experimental work consisted in the arcing of silver by the Bredig process, using conductivity water and chemically pure halides to make up the very dilute solutions. The method was exactly parallel to the one used by Beans and Eastlack⁸, with the exception that silver electrodes were used in place of gold. Otherwise there was no difference, excepting that the electrodes were made of larger wire and greater currents were used. Particular attention was paid to the color of the resulting colloid, the depth of color and the temperature being the controlling factors in the length of time that the arcing was continued. The colloids were examined shortly after formation and again after several days.

The water was prepared by distillation from alkaline permangan-

ate. 10 cc. of 10 per cent NaOH and 10 cc. of a saturated solution of KMnO_4 were put into the five liter round-bottom flask shown in the diagram of the distilling apparatus, Figure 1. The flask was then filled with water from the distilled water tap and capillary air columns^s were inserted to prevent bumping. These were made by drawing out a piece of tubing, sealing one end in a flame and putting the unsealed end down into the solution. They become filled with the liquid after the apparatus is cooled, but may be made ready for use again merely by carefully heating in a Bunsen flame to expell part of the water.

The condenser tube was of block tin surrounded by a Liebig water jacket. It was fitted to the flask by a lead-sheathed rubber stopper, the joint between the glass and the lead being made tight by means of several layers of tin-foil.

The first fourth of the distillate was allowed to escape into the air in order to get rid of most of the ammonia and other dissolved gases and also to lessen the possibility of entraining some of the alkaline permanganate due to the small surface for evaporation when the flask is filled. The water from the next half of the distillate was taken for the experiment. This water was collected with steam coming off of it continuously. This was done by regulating the flow of water in the condenser. The purpose was to prevent absorbtion of the CO_2 and other gases from the atmosphere. Dust particles are also prevented from contaminating the water due to the flow of water vapor away from the mouth of the collecting bottle. The bottles used were cleaned with hot dichromate cleaning solution, rinsed out with distilled water, steamed shoroughly in a steaming apparatus, drained, and rinsed with a little of the condensate from the still,

FIGURE 1

THE DISTILLING
APPARATUS

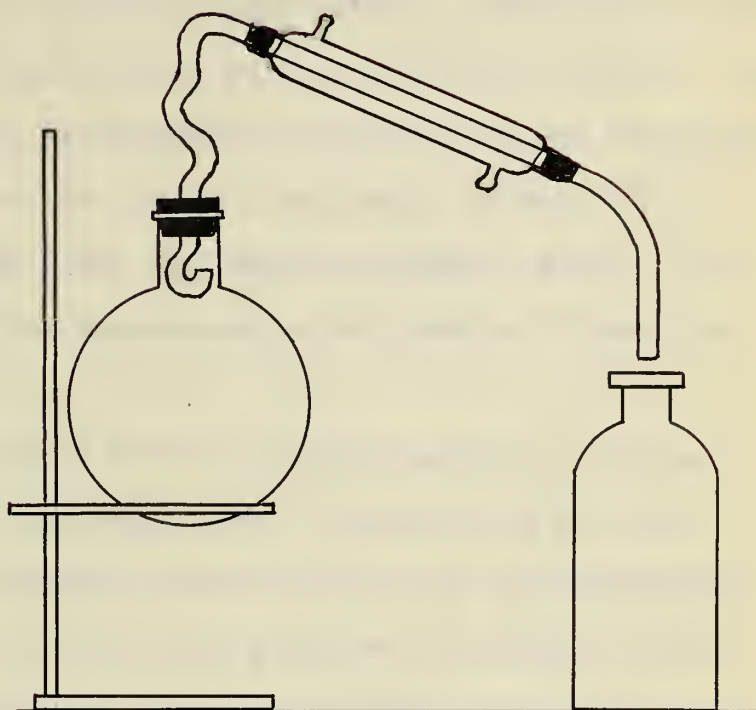
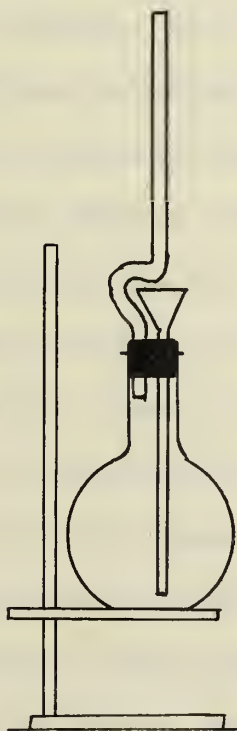


FIGURE 2

THE STEAMING
APPARATUS



before being finally placed to collect the water. When the water was collected, the bottle was covered with tinfoil, previously cleaned with filter paper, and then covered with an inverted beaker. The last quarter of the alkaline permanganate solution was not distilled.

The impurities possible to be present are small amounts of the following: dissolved CO_2 , NH_3 , O_2 , N_2 , $\text{Sn}(\text{OH})_4$, KMnO_4 , NaOH . At no time was any pink color of the permanganate noticeable in the distillate.

Before starting a run, 0.01 N solutions were made up. In the case of hydrogen chloride, chemically pure concentrated HCl was first diluted in a liter volumetric flask to give an approximately 1.0 N solution. This was titrated, using sodium bicarbonate and methyl orange, and the number of cubic centimeters added from a well cleaned burette which when made up to 500 cc. would give a 0.01 N solution. In making up all the other solutions, however, five times the molecular weight of the chemically pure salt expressed in milligrams was added to a well cleaned, steamed, and rinsed 500 cc. volumetric flask, and diluted with thorough shaking to the mark, using conductivity water. To insure a thorough mixture, about 50 cc. were poured out after this and the solution shaken thoroughly again.

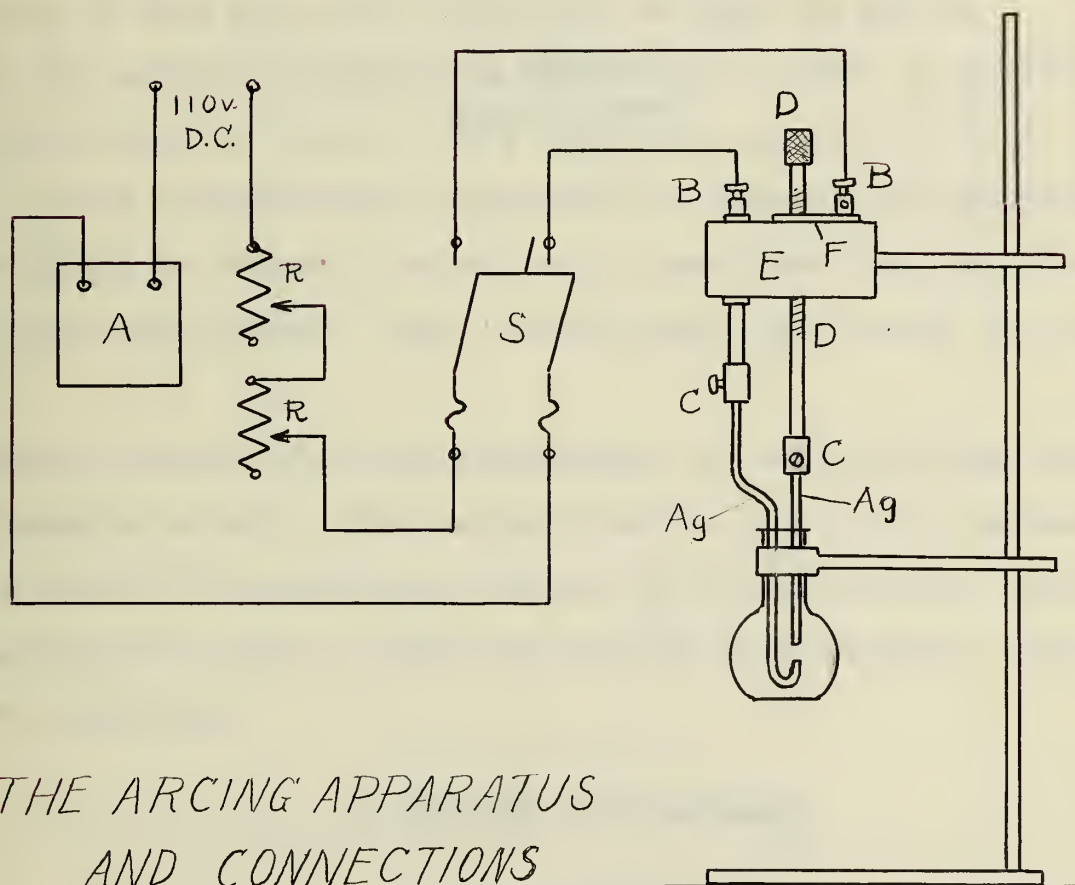
Before making up the various solutions to be used in arcing, it was necessary to have the containers perfectly clean. "Non-sol" Florence flasks of a capacity averaging about 60 cc. were first treated with hot cleaning solution. They were then rinsed with distilled water and steamed thoroughly in the steamer shown in Figure 2. The water in the steaming apparatus was ordinary distilled water and was changed before each experiment. The flasks were then allowed to drain upside down upon filter paper and were finally rinsed

with conductivity water. A 100 cc. volumetric flask and a 30 cc. glass stoppered burette were treated in the same way, the burette of course not being steamed out.

After a few thorough rinsings with the 0.01 N solution, the burette was filled, and the proper volume of solution taken, which when diluted to 100 cc. would give the proper concentration. The following were the normality factors of the solutions made up: 0.0001, 0.0003, 0.0005, 0.0007, 0.0010, 0.0020, 0.0030, 0.0040, and 0.0050. Other strengths were used in some of the experiments. In transferring from the volumetric to a Florence flask, a small volume was first used to rinse the latter container, and then it was tried, owing to the uncertainty of thorough mixing, to transfer an average of the solution by discarding small portions intermittently. In all cases where glass stoppers had to be put down, they were placed upon a double thickness of filter paper. Contact of the fingers with any vital part of the apparatus was of course avoided.

The arcing apparatus is shown in Figure 3. This was almost identical with that used by Beans and Eastlack⁵, excepting for the difference in the size of wire (B. and S., No. 10 was used here) and the absence of glass tube insulators between the wires. The leads were connected to 110 volt, D. C., (110 volt, A. C., will not give more than a flash of an arc). The current passed thru an ammeter A, thence to a two-pole switch, S, set in a block with fuses. The lead from the other pole of the switch passed thru two resistances, R, placed in series and then back to the main, thus leaving the apparatus to be used entirely dead when the switch, S, was open. The switch is connected by wires to brass binding posts, B, which are kept insulated from each other by the ebonite block, E. Silver

FIGURE 3



THE ARCING APPARATUS
AND CONNECTIONS

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wires, Ag, are fastened at C and are bent in the shape shown. The middle electrode is raised and lowered by turning the rod, D, which is connected by a brass plate, F, to one of the binding posts.

Before the apparatus was to be used, the silver electrodes were polished with filter paper, and rinsed with conductivity water. Then another steamed flask with new conductivity water was used for a preliminary arcing to study the formation and stability of the colloid in pure water and conversely to test the water.

In the arcing, electrolysis was avoided as much as possible, although there is bound to be a great deal due to the drop in voltage across the terminals, while the arc exists. The terminals were placed in contact, the circuit closed, and then the electrodes gradually drawn apart. When the arc broke, the switch was pulled open.

In no case was the arcing continued, so that the flask became uncomfortable to hold. The current was from 7.5 to 8.5 amperes giving a drop of voltage across the arc of 30 to 40 volts. The time of arcing for a 60 cc. flask was from 35 to 45 seconds, under the above conditions.

C. Results of Experiment.

Hydrogen Chloride.

Conc. HCl	Color of Sol after Formation		Remarks
	Transmitted Light	Reflected Light	
0.0001 N	Greenish brown	Greenish black	Pptd. in a day
0.0003 } 0.0010 }	Orange red	Light brown	(Not entirely pptd. (in three months
0.0020 } 0.0030 }	Orange red	Very light brown	(Pptd. in two weeks
0.0040 } 0.0050 }	Orange red	Very light brown	(Pptd. in several hours

Additional Notes:- The solutions 0.0030 to 0.0050 immediately became pink and hazy by reflected light and paler in transmitted light. Solutions 0.0003 to 0.0020 took on a greenish yellow fluorescence by reflected light and became pale by transmitted light in a day. The most stable solution was 0.0003, and did not change further even when exposed to sunlight for several months.

Potassium Chloride.

Conc. KCl	Color of Sol after Formation		Remarks
	Transmitted Light	Reflected Light	
0.0001 N	Green-brown	Black	Stable
0.0003) to) 0.0030)	Red wine	Brown with green fluorescence	(Became lighter in color on standing)
0.0040) to) 0.0100)	Red wine	Lighter brown	(Pptd. in several days)

Additional Notes:- These solutions were apparently more stable than the corresponding ones of hydrogen chloride but in time the stability was about the same. The solutions remained brown by reflected light after several days in contrast to those using HCl.

Sodium Chloride.

Conc. NaCl	Color of Sol after Formation		Remarks
	Transmitted Light	Reflected Light	
0.0001 N) 0.0002)	Green brown	Black	Stable
0.0003) to) 0.0020)	Red wine	Brown with green fluorescence	(Became lighter after a few days)
0.0030) to) 0.0090)	Red wine	Lighter brown	(Pptd. in several days)

Additional Notes:- The effects were practically the same as with the corresponding KCl solutions.

Ammonium Chloride.

Conc. NH_4Cl	Color of Sol after Formation		Remarks
	Transmitted Light	Reflected Light	
0.0001	Green Brown	Brown	Pptd. in 2 days
0.0002) to) 0.0007)	Wine red	Reddish brown	(Green to brown (by transmitted (light
0.0010) to) 0.0050)	Reddish yellow	Brownish black	(Pptd. in 2 days

Additional Notes:- The solutions 0.0010 to 0.0050 turned grey by reflected light after several minutes.

Potassium Chloride and Hydrogen Chloride.

Conc. (KCl (HCl	Color of Sol after Formation		Remarks
	Transmitted Light	Reflected Light	
0.0001 N	Green-brown	Green-black	Pptd.
0.0002) to) 0.0010)	Brown-red	Light reddish brown	(Stable but with (appearance like (white of egg
0.0020) to) 0.0050)	Orange red	Light brown turn- ing pinkish	(Pptd.

Additional Notes:- The concentrations are for the total molal concentration, or in other words for the total chloride concentration. The results resembled the use of HCl alone.

Ammonium Chloride and Hydrogen Chloride.

Conc. (NH_4Cl (HCl	Color of Sol after Formation		Remarks
	Transmitted Light	Reflected Light	
0.0001 N	Green	Green-black	Pptd.
0.0002) 0.0003)	Brown	Green brown	Partly pptd.
0.0004) to) 0.0010) 0.0020) to) 0.0050)	Light orange brown Orange brown	Brown Light brown	(Yellow opales- (sence after (several days (A Pptd. leaving (a violet haze

Additional Notes:- The solution 0.0020 took much longer to precipitate than solutions 0.0030 to 0.0050.

Ammonium Chloride and Potassium Chloride.

Conc. (NH ₄ Cl (KCl	Color of Sol after Formation		Remarks
	Transmitted Light	Reflected Light	
0.0001 N	Wine color	Brown black	Stable
0.0002) to) 0.0010)	Wine color	Brown with greenish flor- escence	(Partial pre- (cipitation
0.0020	Orange	Brown	(Slight tinge (after 1 month
0.0030) to) 0.0050	Orange	Light brown	Pptd.

Additional Notes:- The distilled water was tried and acted normally.

Potassium Bromide.

Conc. KBr	Color of Sol after Formation		Remarks
	Transmitted Light	Reflected Light	
0.0001 N	Green brown		Pptd.
1.0003) to) 0.0010)	Orange red	Greenish brown opalescence	(Stable (0.0010 partly (pptd.
0.0020) to) 0.0050)	Orange red	Light brown	Pptd.

Additional Notes:- The color by transmitted light was an orange instead of a wine color.

Potassium Iodide.

Conc. KI	Color of Sol after Formation		Remarks
	Transmitted Light	Reflected Light	
0.0001 N	Brownish green	Green black	Pptd.
0.0003) to) 0.0040)	Dark orange to Light orange	Brown to orange-brown	(Milky (suspension
0.0050	Light orange	Orange-brown	Pptd.

Additional Notes:- It was difficult to get much depth of color with the stronger solutions.

Ammonium Bromide.

Conc. NH_4Br	Color of Sol after Formation		Remarks
	Transmitted Light	Reflected Light	
0.0001 N	Brown	Brown black	Stable
0.0003) 0.0005)	Reddish brown	Green brown	(Partly pptd. (leaves milky (suspension
0.0007) to) 0.0050)	Reddish brown	Green brown	Pptd.

Additional Notes:- The stronger solutions settle out in a few minutes giving a bluish purple precipitate of the photobromide.

Photohalide also appears on the anode. With the chlorides it was first chocolate, then on exposure to light turned pink, red, and finally reddish purple. The photobromide on the anode was first pink and finally became bluish purple. The photoiodide on the electrode was difficult to form; it was first purplish pink and turned to lilac. The tip of the silver cathode was invariably roughened and had a frosted appearance. There was no further effect on the cathode except in the case of the iodide, when a coating of black finely divided silver formed.

The formation of photohalide upon the anode was the heaviest with chloride solutions. Ammonium chloride, unless present with hydrochloric acid will cause this formation to diminish or to disappear entirely. At the same time ammonia seems to contribute greatly to the instability of the colloid as shown in the tables.

D. SUMMARY

1. The colloidal solutions were found to depend for their stability upon the presence of a small amount of electrolyte.

2. The photohalide partly precipitates in a short time from the solutions originally formed leaving a colloidal solution of less concentration.

3. An excess of electrolyte will effect complete precipitation in several days.

4. The photohalides are also formed in the arcing process by electrolytic deposition upon the anode.

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The Design of a Gas Thermoregulator.

During the preliminary experiments, there was occasion to pass hydrogen into a solution of AgNO_3 at a carefully regulated temperature of $55-60^\circ \text{C}$. A Reichert thermoregulator¹ was available, but this was not found to be sufficiently sensitive, although it is claimed to regulate within 2°C . So without reference to the literature, another form was devised, which depends for its operation partly upon the expansion and contraction of air and partly upon the increase and decrease in the vapor tension of a volatile liquid, whose boiling point is slightly above the temperature desired.

The regulator is shown in Figure 4. "B" is a bulb made from a test tube into which is fused a piece of capillary tubing "C" at "a", reaching almost to the bottom as shown. To this is welded at "b", a piece of tubing "A" with two side-arms "D" and "E". The method of filling is to heat the regulator bulb, close the side-arm "E" with a rubber cap and pour in the liquid thru the upper side-arm "D". When the bulb cools, the apparatus is inverted, warmed again, more liquid poured in and the process repeated.

When the bulb was first filled, a few drops of benzene and water were put in, then mercury was added until the level was above the side-arm "E" as shown. The gas was to enter the delivery tube "F" and pass out thru "D" to the burner. The side-arm "E" was intended for use with a setting device and may be dispensed with entirely if such a setting device is not used.

This apparatus is not intended to give a regulation better than 0.5°C . It is sensitive but not delicate, and is devised to be

FIGURE 4

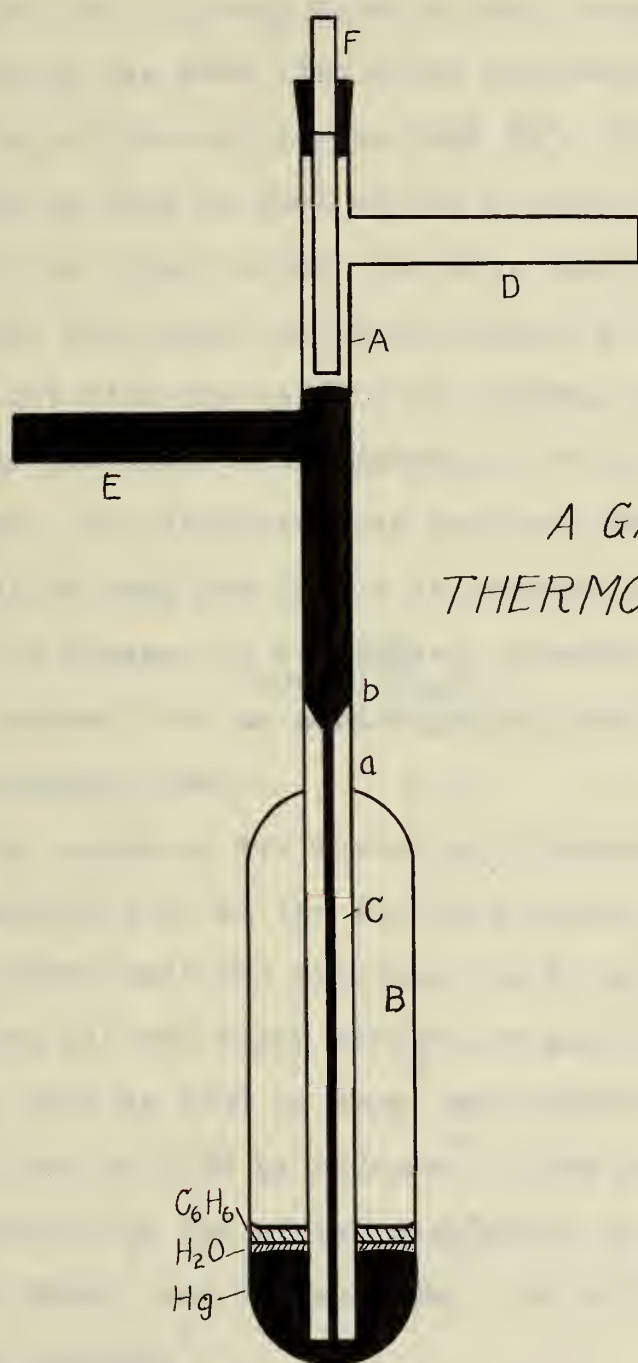


FIG. 1



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portable and to be used in an ordinary beaker of sufficient size.

The advantage lies in being able to use a large flame (an ordinary Bunsen) and at the same time avoid overheating due to the poor conductivity of the air in the bulb "B". The mercury at the bottom will heat up just as fast as the outside liquid; if the lower layers of the liquid become too hot, the mercury will heat up simultaneously and cause the vapor tension of the water and benzene in contact with the mercury to increase suddenly, thereby shutting off the gas while the temperature of the enclosed air has not been changed. The disadvantages are that the apparatus must be kept vertical to keep the "head" of mercury constant, and that it is affected by changes in atmospheric pressure. The former fault could be turned into an advantage and used in the initial setting of the mercury level.

Although this regulator was worked out independently using the Reichert all-mercury type as the starting point, a survey of the literature has shown that the principle is by no means new. This idea of combining air and vapor tension in gas thermoregulators was used as far back as 1850 by Lemp² and improved and modified in 1857 by Bunsen³ and in 1878 by Andreae⁴. Very good descriptions of the construction and use of two regulators of this type are given by Lothar Meyer⁵ and by Kahlbaum⁶. An air thermoregulator is described by Poetsche⁷.

The regulators of this general construction that one sees illustrated and described in the catalogues are of the liquid-mercury type. The Ostwald regulator⁸ uses toluene above mercury, while the Novy type⁹ uses alcohol. The best modern thermoregulator is an electric one devised by Field¹⁰ which uses the principle of com-

binning air and vapor tension and is not affected by changes in atmospheric pressure. Besides these there are the all-mercury and the bi-metallic types.

In looking through the catalogues and abstracts, it seems that the greatest field of modification and duplication is in the part of the apparatus for regulating the flow of gas. In fact some devices described, which the authors no doubt thought original, are almost identical with the earliest forms and possess no advantage over them. This is probably due to this fact that there is no collected bibliography concerning thermoregulators in any journal familiar to the average American scientific worker.

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ACKNOWLEDGEMENT

The writer wishes to extend his sincere thanks to the following gentlemen for their help and assistance: Dr. C. J. Engelder for suggesting the topic of photo-halides and directing the preliminary work, Dr. H. E. Eastlack for suggesting the title subject and the course of the work, and Dr. D. F. McFarland for his assistance in the organization and writing of this thesis.

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